TIME DEPENDENT CHLORIDE DIFFUSION COEFFICIENT – FIELD STUDIES OF CONCRETE EXPOSED TO MARINE ENVIRONMENT IN NORWAY

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Abstract

The apparent chloride diffusion coefficient derived by evaluating chloride profiles using Fick's 2nd law of diffusion is found to be time dependent and may decrease considerably with increasing age of the concrete.

In service life predictions of marine structures this time dependency of the diffusion coefficient is taken into account by an age factor. However, reliable data for this age factor are limited.

Field studies on concrete exposed to marine environment have been conducted in Norway over the last three decades in order to investigate the time dependency of the apparent chloride diffusion coefficient. This paper presents results from some of these field studies.

To illustrate the sensitivity of the age factor in service life calculations, a numerical study is performed using a probabilistic approach.

Key words: Chloride diffusion, ageing, field studies, service life predictions

1. INTRODUCTION

One of the major steps in service life modelling of marine structures has been the insight that the chloride ingress decreases with time. There are several factors which may contribute to this decrease. A main contribution is the effects from cement paste hydration and pore-tightening of the exposed concrete surface layer. Another reason to the observed decrease in the apparent diffusion coefficient over time may be the oversimplification of the chloride ingress model, Fick's 2nd law of diffusion.

By plotting the apparent diffusion coefficients against time in a log-log scale the trend line of the fitted diffusion coefficients seems to yield a straight line. A commonly used empirical expression for the time dependent diffusion coefficient in Fick's 2nd law has been:

$$D(t) = D_0(t_0/t)^{\alpha} \quad (1)$$

Where
- $D(t)$ = apparent diffusion coefficient after exposure time t

- D_0 = initial diffusion coefficient after time t_0
- α = the age factor

Several investigations have been conducted world wide to stipulate the age factor, α, and many different values have been found in the literature. Most of the values are based on data from a relative short exposure period or from different marine structures with different concrete compositions and under varying exposure conditions. Systematic long term field investigations suitable for determine reliable data for this ageing effect are very limited.

Field studies on chloride intrusion have been conducted in Norway over the last three decades in order to investigate the time dependency of the apparent chloride diffusion coefficient. This paper presents results from some of these field studies. Further, probabilistic service life calculations are performed in order to illustrate the sensitivity of the age factor on the achieved service life.

2. MARINE FIELD STUDIES

2.1 Test programmes

A review of the available Norwegian field studies is given in /1/. Only a subset of these field studies is found suited for studying the ageing effect. These studies are listed in Table 1. The binders consisted of CEM 1 and varying amount of reactive additives (silica fume, fly ash and blast furnace slag). Both normal density (ND) concrete and light weight aggregate (LWA) concrete were studied. The water-binder ratio varying from 0.37 to 0.45 for the ND concretes. The water-binder ration was somewhat lower for the LWA concretes (0.29-0.40).

Table 1: Norwegian marine field studies applied to investigate time dependency of the apparent diffusion coefficient

Study No	Field study location	Exposure year	Test periods	Concrete	Exposure
1	Østmarkneset (Test blocks)	1983	1 ½, 5, 9 14, 21 ½ years	ND	Tidal zone
2	Østmarkneset (Test blocks)	1992	1, 5, 9 years	LWA	Immersed/ Tidal zone
3	Kristiansand (Test cubes)	1997	35, 200, 700 days	LWA	Immersed/ Tidal zone
4	Østmarkneset (Test cylind.)	1998	35 days, 200 days, 1, 2, 5, 9 years	ND	Tidal zone
5	Brevik (Test cylinders.)	1999	35 days, 200 days, 1, 2, 5, 10 years	ND	Immersed
6	Oslo fjord (Test cubes)	1999	7, 28, 145, 230, 400, 750 days	ND	Immersed

For all the field studies concrete test blocks, cubes or cylinders were exposed to marine environment, either located in the tidal zone or immersed in sea. Some parallel test cubes were also located in laboratory immersed in sea water. At different time intervals sampling of the test specimens were performed and analysed for chloride ingress. For each concrete a unique time series of the chloride ingress into this concrete is then obtained. These test series are studied further in this paper.

The most comprehensive and reliable data material can be found in field study No 4 and 5. These studies include 10 different normal density concrete recipes with CEM I. The fly ash content varied from zero to 20 % by weight of cement. The same recipes have been applied for both studies, but the exposure conditions were different. In study 4 the test specimens were exposed in the tidal zone, whereas in study No 5 the specimens where immersed in the sea. Different from most available field studies, all testing have been performed according to the same procedures (i.e. grinding of thin layers from the test specimens and chloride analyses of the ground layers by a spectrophotometric method) and by the same laboratory through the whole exposure period of 9 and 10 years, respectively.

2.2 Calculated surface chloride concentration and diffusion coefficient

The apparent coefficient for chloride diffusion, D, and the theoretical (calculated) chloride surface concentration (C_0), after each exposure period, are calculated from the measured chloride profile by applying a best curve fit using the error function solution of Fick's 2nd law of diffusion, according to Equation 2:

$$C(x,t) = C_0 - (C_0 - C_i)\,\mathrm{erf}\left(x/\sqrt{4 \cdot D(t) \cdot t}\right) \qquad (2)$$

Where:
- $C(x,t)$ = chloride content in distance x from the surface after exposure time t
- C_i = initial concrete chloride content
- erf = error function

Some results from the field studies 4 and 5 are shown in Figure 1 and 2. Figure 1 shows calculated values of C_0 for comparable CEM I - normal density (ND) concretes, with and without fly ash. Corresponding values for the apparent diffusion coefficients (D) are plotted in Figure 2.

From Figures 1 and 2 it can be seen that both C_0 and D are time dependent. The surface chloride concentration increases with time whereas the apparent chloride diffusion coefficient declines. In spite of large variations within the data material, there are two obvious trends. The long term development for samples exposed in the tidal zone is different than the development for samples immersed in sea water. There is also a significant difference between samples with and without fly ash. Similar results are found for the other ND concretes.

For the long term field study No 1, no reduction in apparent chloride diffusion coefficient could be observed from 14 till 21 ½ years.

The data material for light weight aggregate (LWA) concrete is limited. Nevertheless, it was observed that the difference between immersed and tidal zone exposed samples with the regard to long term development of C_0 and D is similar to the ND concretes. The level of the chloride content is, however, much higher for the LWA concretes.

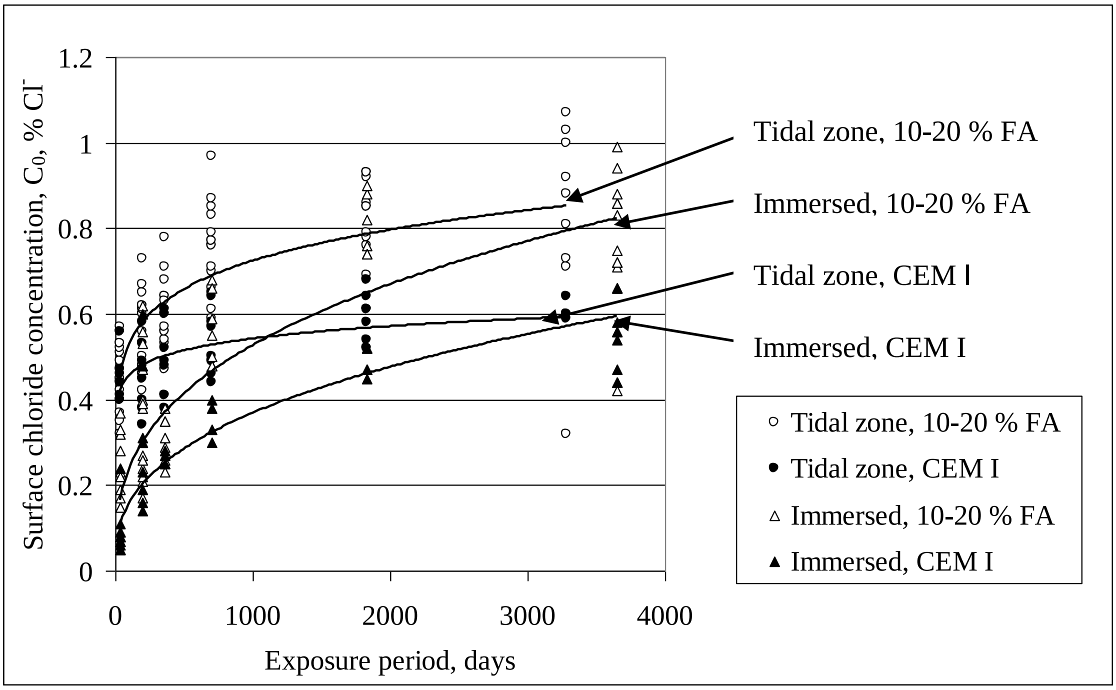

Figure 1: Surface concentration (C_0) in % of concrete weight for ND concrete with and without fly ash (FA). Results based on study No 4 and 5.

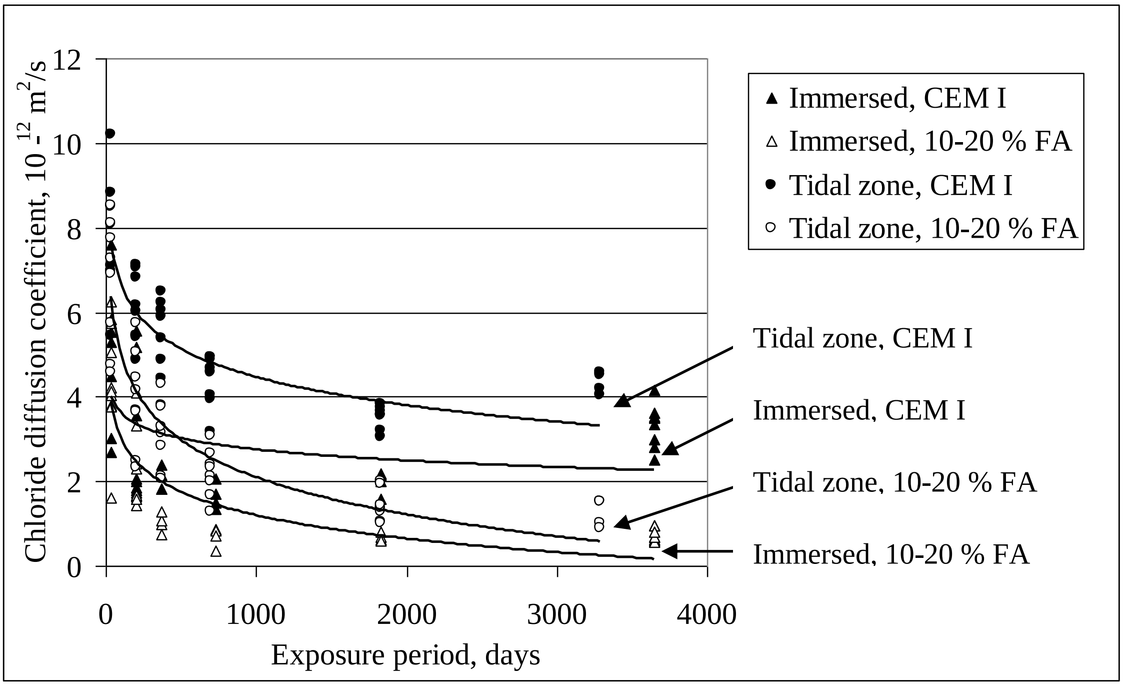

Figure 2: Apparent diffusion coefficient (D) for ND concrete with and without fly ash (FA). Results based on study No 4 and 5.

2.3 Age factor, α

For each of the measured time series the apparent diffusion coefficient the age factor, α, (see Equation 1) has been calculated by a regression analysis. The mean values and standard deviation for the different concretes and exposure conditions derived from the Norwegian field studies are shown in Table 2.

Table 2: Calculated age factors, α, from Norwegian field studies. (Mean values and standard deviation). Number of test series in brackets

Concrete [1)]	**Exposure condition**	**Marine environment**		**Immersed in sea water in laboratory**
		Tidal zone	**Submerged zone**	
Light weight aggregate (LWA) concrete	CEM I with 5-10 % SF	0.56±0.16 (5)	0.49±0.14 (5)	0,59±0.04 (4)
	CEM I with 5-10 % SF and 50 % gbf slag			0,75±0.11 (4)
Normal density (ND) concrete	CEM I	0.19±0.03 (9)	0.10±0.04 (8)	
	CEM I with 8-10 % SF	0.38±0.00 (2)		0.47 (1)
	CEM I with 20 % SF	0.43±0.06 (2)		
	CEM I with 10-20 % FA	0.40±0.04 (12)	0.41±0.09 (14)	0.45 (1)
	CEM I with 35 % FA	0.52±0.06 (2)	0.41±0.13 (2)	
	CEM I with 4-5 % SF and 20 % FA	0,46±0.08 (2)	0.37±0.02 (3)	0.54 (1)
	CEM I with 8-10 % SF and 20 % FA		0.45 (1)	0.45 (1)

[1)] Silica fume (SF), blast furnace (gbf) slag and fly ash (FA) are given in % of cement weight.

2.4 Discussion

A general observation is that the calculated surface chloride concentration, $C_{0,}$ and the apparent chloride diffusion coefficient, D, is time dependent and seems to reach a constant value after approximately 10-15 years of exposure, depending on concrete types and environmental conditions. As C_0 and D are dependent variables, it may be concluded that treating C_0 as a constant value in the solution of Fick's 2^{nd} law of diffusion, the calculated apparent coefficient may not be correct. Moreover, the empirical derived Equation 1, modelling the time dependency of the diffusion coefficient, is only valid within range covered by the measured data, and an extrapolation may give non-conservative results.

For normal density CEM I concretes the age factor is in the order of 0.1 - 0.2 depending of expose condition (tidal or submerged zone). This is considerably lower than the corresponding values for concrete with fly ash and/or silica fume. For concretes containing silica fume and/or fly ash the mean value of the observed age factor in marine environment is approximately 0.4.

The age factor obtained for LWA concrete seems to be somewhat higher compared to ND concrete. However, for the investigated LWA concretes, the chloride surface concentration, C_0, and the apparent diffusion coefficient, D, were much higher than observed for the ND concretes. Thus, the age factors for ND and LWA concrete have to be treated separately.

In Table 3 the age factors obtained after 9 years of exposure based on the Norwegian field study No 4, are compared with values recommended in ***fib*** Model Code for Service Life Design [2] and Dutch Guidelines as presented in [3]. As observed the age factors found in the Norwegian field study are lower than the values recommended in [2] and [3]. It is worth mentioning that the results from the Norwegian field studies are not included in the statistical quantification or evaluations underlying the recommendations presented in [2] and [3].

The uncertainties related to the age factor and its influence on achieved service life of marine structures is further discussed in the next chapter.

Table 3: Age factor, α, for CEM 1 and FA concretes in the tidal zone (mean values)

Type of binder	**Norwegian field study (9 years of exposure)**	**Recommendations:**	
		***fib* Model Code for Service Life Design**	**Dutch Guidelines**
CEM 1	0.19	0.30	0.40
CEM 1 with10-20 % FA	0.40		
CEM I >20% FA	0.52	0.60	0.70

3. SERVICE LIFE PREDICTIONS

In order to illustrate the impact of the age factor on the prediction of service life of marine structures a sensitivity study has been performed. A probabilistic approach has been applied in order to include the uncertainty of the parameters in a consistent manner. The calculations are performed based on Equations 1 and 2. The limit state function is defined as the difference between the critical chloride concentration and the calculated chloride concentration at the surface of the reinforcement:

$$g(X) = C_{cr} - C(x,t) \qquad (3)$$

where X is a vector of the statistical parameters.

In this sensitivity study only the apparent diffusion coefficient D and age actor α are treated as statistical variables. The set of statistical variables used in the numerical study are listed in Table 4.

The calculations are based on a design service life of 50 years. The acceptance criterion is set to 10 % probability to onset of corrosion.

Fixed or characteristic values are used for the remaining model parameters. For the surface chloride concentration, C_0, a fixed value of 1.0 % of concrete weight is used. This should be a reasonable long term value for the fly ash concrete shown in Figure 1. For the critical chloride concentration, C_{cr}, a characteristic value of 0.10 % of concrete weight is used. This has shown to be a reasonable characteristic value for onset of corrosion based on an acceptance criterion of 10 % probability of corrosion, [4].

Table 4: Statistical input parameters to the service life calculations

Statistical parameters	**Mean**	**Coefficient of variation, CoV**
Apparent diffusion coefficient, D [m^2/s]	$7.0 \cdot 10^{-12}$	15 %
Age factor, α	0.4	10 % and 15 %
	0.6	10 % and 15 %

The results of the numerical study are shown in Figure 3 for the two value of the age factor 0.4 and 0.6, respectively. As seen, the age factor is a very dominant parameter in the service life predictions. The deterministic approach, i.e. using the mean value of the age factors, corresponds to the concrete cover at 50 % probability of corrosion.

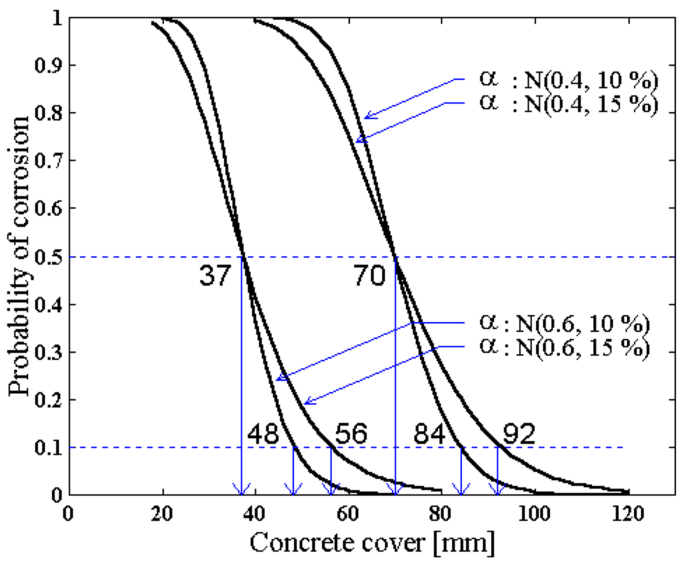

Figure 3: Calculated concrete cover for different statistical parameters of the age factor, α, for a design service life of 50 years.

Using an acceptance limit of 10 % probability to corrosion initiation and an age factor of 0.6, the concrete cover becomes 48 and 56 mm, respectively, for a CoV of 10 % and 15 %.

Reducing the age factor to 0.4 the concrete covers have to be increased by 36 mm, to 84 and 92 mm, in order to achieve the design service life of 50 years.

The type of concrete binder will obviously affect both the apparent diffusion coefficient and the surface chloride concentration. Further sensitivity studies, but not reported here, have shown that these effects are minor compared to the effect of the age factor on the service life predictions.

4. CONCLUSIONS

A general observation from the Norwegian marine field studies is that the calculated surface chloride concentration C_0 and the apparent chloride diffusion coefficient D is time dependent and seem to reach a constant value after about 10 -15 years of exposure, depending on concrete types and environmental conditions.

For normal density CEM I concretes the age factor is found to be in the order of 0.1 - 0.2, depending of exposure condition (tidal or submerged zone). This is considerably lower than the corresponding values for concrete with fly ash and/or silica fume. For concretes containing silica fume and/or fly ash the mean value of the observed age factor in marine environment is approximately 0.4.

The age factor, α, obtained for LWA concrete seems to be somewhat higher compared to ND concrete. However, for the investigated LWA concretes, the chloride surface concentration, C_0, and the apparent diffusion coefficient, D, were much higher than observed for the ND concretes. Thus, the age factors for ND and LWA concrete have to be treated separately.

Using the empirical Equation 1 to model the time dependency of the apparent diffusion coefficients, it is vital that the value of the age factor is representative for the time period of interest, as the age factor in this study is found to decrease over time.

The age factor is a very sensitive parameter in the service life prediction. The probabilistic calculations showed that a concrete cover of about 50 mm is needed using a mean value of the age factor of 0.6. Reducing the age factor to 0.4, the concrete cover has to be increased by 36 mm in order to achieve the same design service life of 50 years.

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